

A new nonlinear stochastic Liouville equation

Inclusion of finite relaxation and finite temperature effects

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Abstract. A nonlinear stochastic Liouville equation postulated phenomenologically and used recently for the description of the interplay of damping and nonlinearity is shown to arise in a natural manner as an approximate consequence of a set of Langevin equations introduced for the analysis of the Brownian motion of a nonlinear quantum dimer. The validity of the phenomenological equation is discussed in the light of the approximate derivation. A more physical transport equation for the system density matrix is obtained and shown, on the one hand to reduce to the phenomenological equation in an appropriate high temperature limit, and on the other to predict novel behavior. The new nonlinear stochastic Liouville equation we present is capable of unifying the description of the nonlinear transport of quasiparticles in several different parameter regimes and we suggest that it should be regarded and used in the same role in the study of the physics of nonlinear transport phenomena that the linear stochastic Liouville equation does in fields such as (linear) exciton dynamics in molecular crystals and aggregates.

1. Introduction

Recently, a discrete nonlinear stochastic Liouville equation (SLE) was introduced for the study of the interplay of damping and nonlinearity and investigated for its effects on neutron scattering and time evolution on the one hand and its Painlevé properties on the other [1]. The equation was formulated by adding dephasing terms to the discrete nonlinear von Neumann equation [2]. The dephasing terms were taken to destroy off-diagonal terms of the density matrix ρ (in the representation of site states m, n , etc.) at a constant rate α in the standard manner [3–7] as explained by Reineker [3] and others. The resulting nonlinear adiabatic stochastic Liouville equation had the form

$$id\rho_{mn}/dt = [V, \rho]_{mn} - \chi(\rho_{mm} - \rho_{nn})\rho_{mn} - i\alpha(1 - \delta_{mn})\rho_{mn} \quad (1)$$

which, for the dimer (two-site system in which m, n take on values 1 and 2 only) studied in [1] reduced to

$$dp/dt = 2Vq \quad (2a)$$

$$dq/dt = -2Vp - \chi pr - \alpha q \quad (2b)$$

$$dr/dt = \chi pq - \alpha r \quad (2c)$$

where the real quantities p, q, r are obtained from the density matrix elements through

$$p = \rho_{11} - \rho_{22}; \quad q = i(\rho_{12} - \rho_{21}); \quad r = (\rho_{12} + \rho_{21}). \quad (3)$$

The evolution predicted by (2) is seen [1] to exhibit the nonlinear elliptic function oscillations characteristic of the nonlinear adiabatic dimer [8] at short times but to tend to equal population on the two sites at long times as a consequence of the dephasing introduced by α . A considerably more satisfactory description of damping was given more recently by Kenkre and Wu [9] simply by relaxing the adiabatic approximation, i.e., by refraining from making the assumption that vibrational relaxation, which leads to the nonlinearities in the discrete nonlinear Schrödinger equation, is infinitely fast. No ad hoc terms such as $-\alpha q$ and $-\alpha r$ in (2) were introduced. Among the physical results obtained for this *nonadiabatic* evolution was the long-time settling of the system into the stationary states of the *adiabatic* dimer. Questions that remain unanswered are: is there a relation between the adiabatic SLE used in [1] and the results of the nonadiabatic analysis of [9]? Is it possible to derive or justify the adiabatic SLE (which was introduced merely phenomenologically in [1]) from a more acceptable starting point? And what is the extent of its validity and applicability? This paper consists of answers we have found to these questions from a theory developed recently [10] for the description of the Brownian motion of the nonlinear dimer. A useful and important byproduct of our attempts to answer the questions is a new nonlinear stochastic Liouville equation which is much

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more physical than the adiabatic SLE but reduces to it in an appropriate limit. We present and discuss the new SLE and compare its predictions with those of its adiabatic counterpart.

The system we describe is, as said above, a quasiparticle moving between two sites 1 and 2. Its respective amplitudes are c_1 and c_2 , and its intersite transfer interaction is V . The nonlinearities in its evolution arise from its coupling with oscillators at the two sites with displacements x_1 and x_2 , and frequency ω . The interaction with the quasiparticle shifts the equilibrium position of each oscillator from zero by an amount proportional to the probability of occupation of the respective site by the quasiparticle, and the oscillator motion is damped. The system is treated in the limit that the damping rate and the oscillator frequency are large enough so that one need consider only a single relaxation time $1/\Gamma$ which is proportional to the ratio of the damping rate to the square of the frequency. Specifically, the starting point [9] in the absence of further dephasing or stochastic interactions would be

$$i dc_1/dt = Vc_2 + Ex_1 c_1 \quad (4a)$$

$$i dc_2/dt = Vc_1 + Ex_2 c_2 \quad (4b)$$

$$dx_1/dt + \Gamma x_1 = -(\chi\Gamma/E)|c_1|^2 \quad (4c)$$

$$dx_2/dt + \Gamma x_2 = -(\chi\Gamma/E)|c_2|^2 \quad (4d)$$

χ being a measure of the nonlinearity, and E an interaction constant. In the present investigation we are interested in finding out whether the origin of (2) with appropriate modifications, if necessary, can be understood from (4) when stochastic forces arising from interactions with a bath are added to the system. The idea is to obtain, if possible, a transport equation similar to that obtained [3–7] earlier for exciton dynamics but capable of addressing *nonlinear* transport. The required tools are provided by a recent formalism constructed by Grigolini et al. [10]. On adding stochastic forces F_1 , and F_2 which are Gaussian white noises given specifically by

$$\langle F_m(0) F_m(t) \rangle = 2\Gamma \langle x_m^2 \rangle_{\text{eq}} \delta(t) = 2\Gamma (k_B T/\omega^2) \delta(t) \quad (5)$$

to the right hand sides of (4c) and (4d) above, one finds in [10] the following Fokker-Planck equation in the limit of large relaxation (Γ much larger than all other rates such as χ and V):

$$\partial \sigma(p, q, r; t) / \partial t = L_{\text{red}} \sigma(p, q, r; t) \quad (6a)$$

$$\begin{aligned} L_{\text{red}} = & L_q + (2V/\Gamma)(\chi q)[q(\partial/\partial r) - r(\partial/\partial q)] \\ & + (2\chi k_B T/\Gamma)[(\partial^2/\partial q^2)r^2 - (\partial/\partial q)r(\partial/\partial r)q \\ & - (\partial/\partial r)q(\partial/\partial q)r + q^2(\partial^2/\partial r^2)] \end{aligned} \quad (6b)$$

Here $\sigma(p, q, r; t)$ is the reduced distribution function which describes the evolution of the quasiparticle alone (obtained by eliminating the oscillator variables), L_{red} is the corresponding reduced Fokker-Planck operator, T is the temperature and k_B the Boltzmann constant. Of the terms in the operator L_{red} , L_q which is given by

$$L_q = 2V[p(\partial/\partial q) - q(\partial/\partial p)] + \chi p[r(\partial/\partial q) - q(\partial/\partial r)] \quad (7)$$

refers to the *adiabatic* evolution of the quasiparticle while the other parts describe the effects of the nonadiabaticity.

2. The new nonadiabatic nonlinear stochastic Liouville equation

In [10], Eq. (6) have been used to obtain further reduced Fokker-Planck equations and to calculate escape rates through a generalized Kramer's analysis. In the present paper, our interest is in obtaining evolution equations for the average quantities $\langle p \rangle$, $\langle q \rangle$ and $\langle r \rangle$. On multiplying (6a) by p , q , and r respectively and carrying out an integration over those variables, we find, as an *exact* consequence of (6), the following set of coupled equations:

$$d\langle p \rangle/dt = 2V\langle q \rangle \quad (8a)$$

$$d\langle q \rangle/dt = -2V\langle p \rangle - \chi\langle pr \rangle + (2V\chi/\Gamma)\langle qr \rangle - \alpha\langle q \rangle \quad (8b)$$

$$d\langle r \rangle/dt = \chi\langle pq \rangle - (2V\chi/\Gamma)\langle q^2 \rangle - \alpha\langle r \rangle \quad (8c)$$

where the “dephasing” rate α is given by

$$\alpha = (2/\Gamma)(E/\omega)^2 (k_B T) = (2\chi/\Gamma)(k_B T). \quad (9)$$

The second equality in (9) is obtained by realizing that (4c) is the high-damping limit of

$$d^2 x_1/dt^2 + (\omega^2/\Gamma)(dx_1/dt) + \omega^2 x_1 = -E|c_1|^2 \quad (4c')$$

(similarly for (4d)), and that therefore $(E/\omega)^2 = \chi$ holds.

Equations (8) constitute one of the new results of the present analysis. In order to derive a result which is both more useful and more easily comparable to (2) above, it is necessary to evaluate the quantities $\langle qr \rangle$, $\langle pr \rangle$ and $\langle pq \rangle$ in (8). A simple factorization approximation such as $\langle pr \rangle \approx \langle p \rangle \langle r \rangle$ is too crude and leads to unphysical results. We employ, instead, the following approximation:

$$\begin{aligned} \langle p^a q^b r^c \rangle_t \approx & \langle p \rangle_t^a \langle q \rangle_t^b \langle r \rangle_t^c \\ & + [\langle p^a q^b r^c \rangle - \langle p \rangle^a \langle q \rangle^b \langle r \rangle^c]_{\text{eq}} \end{aligned} \quad (10)$$

where a, b, c are appropriate numbers (1 or 2 for our use here) and the symbols t and *eq* denote, respectively, the values at time t and in equilibrium respectively. The equilibrium solution σ_{eq} of (6) is straightforward to obtain:

$$\sigma_{\text{eq}}(p, q, r) = N_c \exp\{- (V/k_B T)[r - (\chi/4V)p^2]\}. \quad (11)$$

N_c being a normalization constant. The substitution of (10) in (8) and the use of (11) for the evaluation of the equilibrium averages with the help of (11) reduces (8) to

$$dp/dt = 2Vq \quad (12a)$$

$$dq/dt = -2Vp - \chi pr + (2V\chi/\Gamma)qr - \alpha q \quad (12b)$$

$$dr/dt = \chi pq - (2V\chi/\Gamma)q^2 - \alpha[r - r_{\text{eq}}] \quad (12c)$$

where we have used the notation p, q, r , to denote $\langle p \rangle$, $\langle q \rangle$, $\langle r \rangle$ respectively in order to make comparison with

(2) easier. The term r_{eq} in (12c) appears as a natural consequence of the calculation. Two remarks appear to be appropriate at this stage. The first is that (11) which describes the steady state solution of the Fokker-Planck equation (6), (7), can be obtained through the contraction of the steady state solution of the full Fokker-Planck equation (see, e.g. (2.6)–(2.9) of [10]) for the complete distribution $\rho(p, q, r, z)$ which includes z , an appropriately normalized difference of the oscillator displacements x_1 and x_2 . This more complete solution, which we have not presented earlier, is

$$\rho(p, q, r, z) = \text{constant} \cdot \exp\left\{-\frac{V}{k_B T}\right\} \cdot [r - (\chi/4V)p^2] \cdot \exp\left\{-\frac{\chi z^2}{2k_B T}\right\}$$

and the process of contraction consists of an integration over z . The second remark is that the quantity $V[r - (\chi/4V)p^2]$ whose canonical distribution is described by (11), and which, except for additive constants, is the energy-like slow variable chosen in [10] and [11], is nothing other than the energy of a dipole interacting with a magnetic field whose transverse component depends on the dipole moment. This magnetic analogy has interesting consequences which we will discuss elsewhere.

The nonlinear stochastic Liouville equation (12) is the central result of this paper. Although it suffers from the limitations of the factorization approximation (10) made to derive it from (8), it has considerable physical content. It reduces to several cases studied earlier in appropriate limits. If there is no coupling of the quasiparticle with the oscillators, all terms on the right side of (12c) and all but the first term on the right side of (12b) vanish, and the linear dimer is recovered. If the vibrational relaxation rate is infinitely large, the two last terms on the right side of (12b) as well of (12c) vanish, and the nonlinear adiabatic dimer [8] is recovered. If the temperature T is taken to be zero, α in (9) disappears, the last terms in (12b) and (12c), which describe pure decay (dephasing), vanish, and the nonadiabatic dimer of [9] is recovered. Finally, if χ/Γ is small but $k_B T/\Gamma$ is not small, the nonadiabatic terms in (12b) and (12c), viz. $(2V\chi/\Gamma)qr$ and $(2V\chi/\Gamma)q^2$ respectively, vanish, and one recovers, except for the term r_{eq} in (12c), (2) above, i.e. the nonlinear adiabatic stochastic Liouville equation of [1], whose range of validity prompted this investigation. The difference regarding r_{eq} arises from the well known fact that the ordinary SLE leads to incorrect thermalization [5, 8], and that consequently (8) which is a straightforward extension of that SLE, is inappropriate at temperatures which are not too large. The term r_{eq} in (10) disappears in the limit of infinite temperature.

3. Time evolution and comparison with the adiabatic SLE

The nonlinear SLE we have derived in this paper, viz. the set of (12), has striking predictions whose meaning can be understood clearly from the physics of the system. We display these in Figs. 1–3 below. The comparison of the predictions of (12) with those of the earlier SLE (2) is made pictorially in Figs. 4, 5. All solutions are

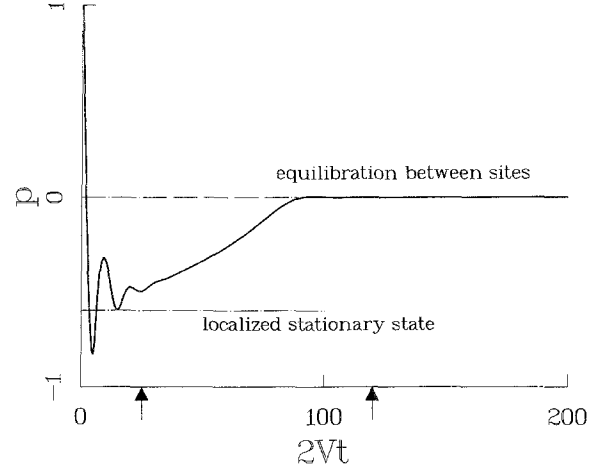


Fig. 1. Time evolution in the dimer as predicted by the new nonlinear stochastic Liouville equation presented in this paper: the difference $p(t)$ of site occupation probabilities in the nonlinear nonadiabatic dimer at finite temperatures is plotted as a function of the dimensional time $2Vt$, for the condition that a single site is occupied initially. Two separate processes in the evolution of the quasiparticle, viz. the formation of the self-trapped state (equivalently the polaron) and its later destruction as a result of thermal fluctuations, are seen clearly. Arrows mark the different time regimes. The localized state value of p is obtained from the expression $p^2 = 1 - (2V/\chi)^2$ to be found in [2, 8, 10]. Parameter values, in units of $2V$, are: $\chi = 1.25$, $\Gamma = 3$, and $\alpha = 4 \times 10^{-3}$. These represent the nonlinearity, vibrational relaxation, and temperature dephasing, respectively

obtained numerically from (12) and (2) through a straightforward fourth-order-Runge-Kutta algorithm. We also assume, for the sake of simplicity, that the temperature is high enough to justify the neglect of r_{eq} in (12c).

In all figures, the probability difference between the two sites in the dimer, viz. $p(t)$ is plotted as a function of time t , in units of $1/2V$, for the condition that only one of the sites is occupied initially. We see in Fig. 1, that the system settles first in one of its localized (self-trapped) states when t reaches approximately the value $10/V$. We also see that the system subsequently leaves this state and equilibrates between the two self-trapped states in times of the order of $50/V$. The two time regions have been marked by arrows in Fig. 1. The first process is the formation of the polaron, and has been obtained, displayed and discussed in [9]. The second process is the over-barrier hopping discussed in [10]. Both its time evolution and its coexistence with the first process (self-trapping) seen clearly in Fig. 1, are new features of our analysis which, to our knowledge, have not been displayed earlier in the literature. The nonlinear SLE we present provides a single transport instrument capable of describing in a unified fashion both the formation of the nonlinear structure (the polaron) as a result of the strong interaction with the vibrations, and its destruction as a result of thermal fluctuations. The nonlinearity ratio $\chi/2V$ in Fig. 1 has been chosen to be 1.25 which is intermediate between the “static” and “dynamic” transition values 1 and 2. The value 1 characterizes

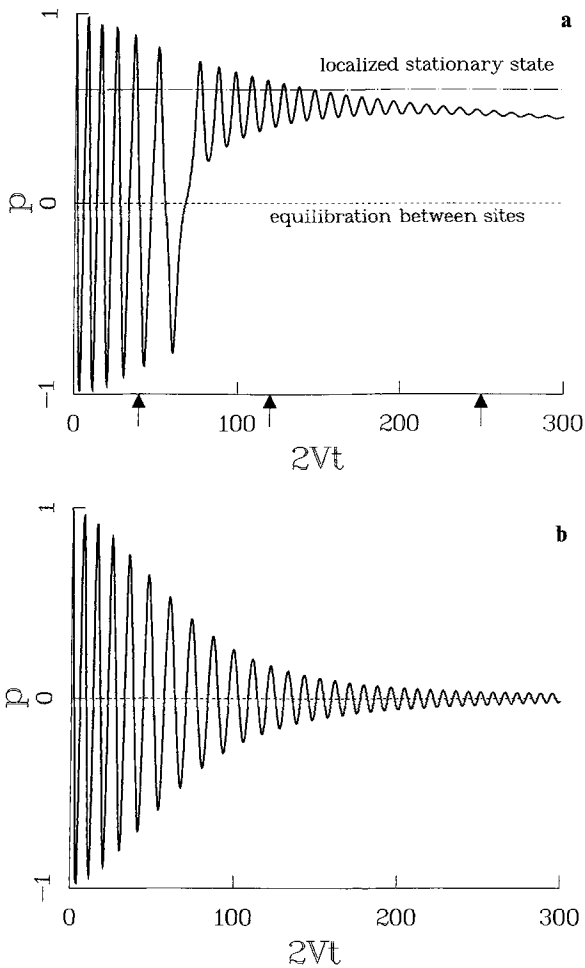


Fig. 2a, b. The site occupation probability difference $p(t)$ plotted as in Fig. 1 for the same value of nonlinearity ($\chi/2V=1.25$) as in Fig. 1 but for a larger relaxation rate ($\Gamma/2V=30$). The dephasing rate α equals 0.4×10^{-3} in **a** and 6.4×10^{-2} in **b** (in units of $2V$). In **a**, a preliminary stage, in which no self-trapping tendencies are seen, is followed first by self-trapping and then by the beginning of equilibration between the two sites, i.e. of the destruction of the localized state. The higher value of the dephasing rate α in **b**, however, hides the formation of the localized state altogether

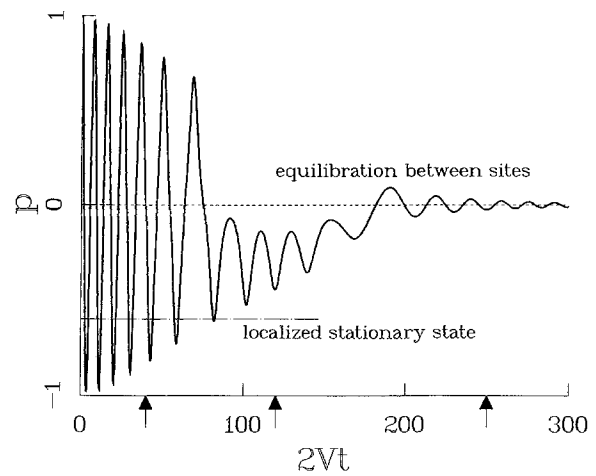


Fig. 3. The evolution of $p(t)$ as in Fig. 2, with the same values 1.25 and 30 (in units of $2V$) for the nonlinearity ratio χ and the relaxation rate Γ , respectively, but for a value of the dephasing rate α which is intermediate ($\alpha/2V=1.6 \times 10^{-3}$) between those in Fig. 2a and b. All three phases of the evolution are clear in this case: the pre-selftrapping oscillations, the formation of the localized state, and its destruction resulting in the equilibration between the two sites

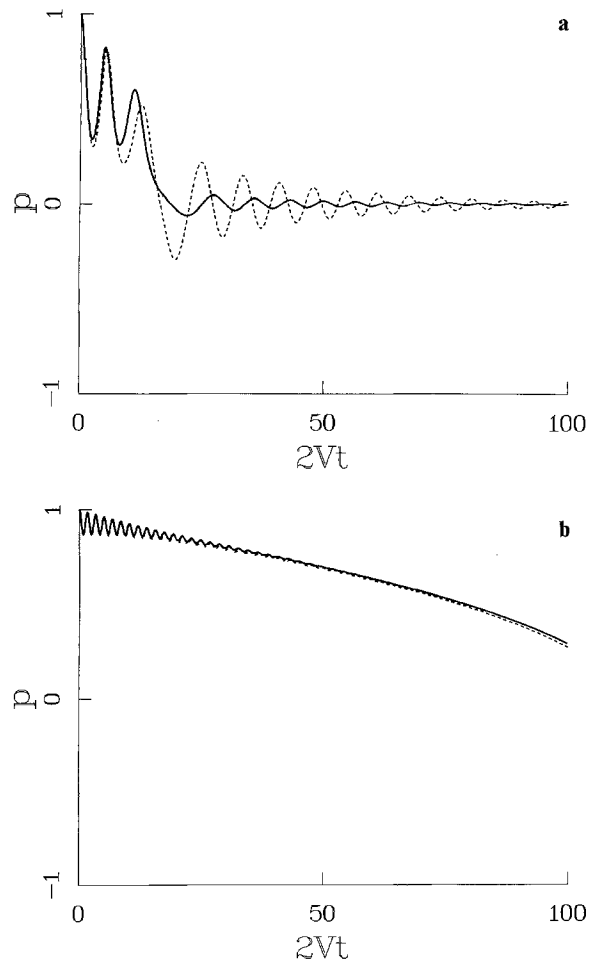


Fig. 4a, b. Comparison of the predictions of the new *nonadiabatic* SLE presented in this paper (12) with those of the old *adiabatic* SLE (2). The site occupation probability difference $p(t)$ is plotted for the initial condition that a single site is completely occupied. Here and in Fig. 5 below, solid lines denote the evolution as described by the new SLE while dashed lines represent the old SLE. The relaxation is taken to be fast ($\Gamma/2V=40$) and the dephasing rate α is 6.4×10^{-3} in units of $2V$. **a** and **b** differ in the value of the nonlinearity: $\chi/2V$ equals 2.1 in **a** but 4 in **b**. Not much qualitative difference exists between the old SLE and the new SLE in this case

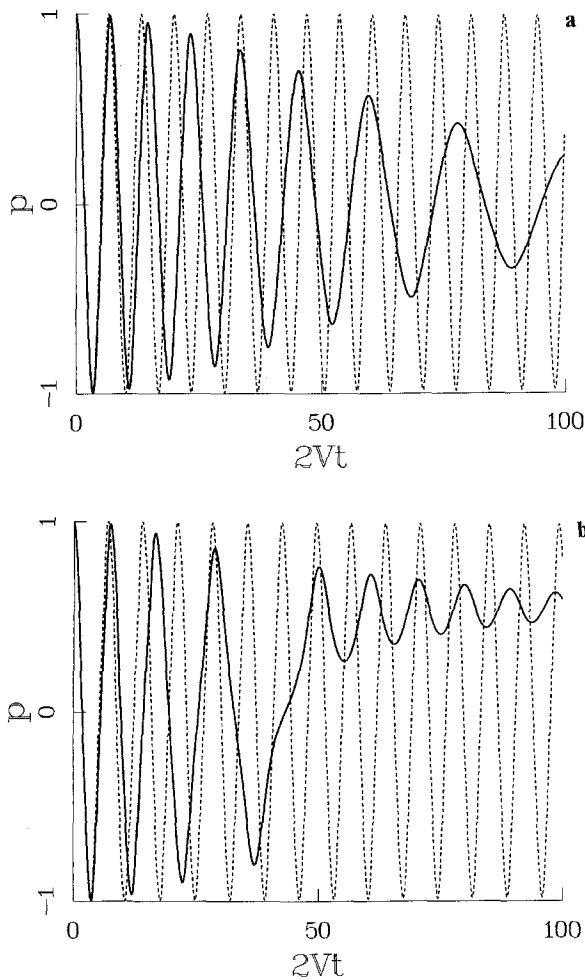


Fig. 5a, b. Comparison of the two SLE's as in Fig. 4 in another parameter regime. The relaxation rate Γ is 20 in units of $2V$, and the dephasing rate α is 4×10^{-4} . Both are slower than in Fig. 4. The nonlinearity ratio $\chi/2V$ equals 1 in **a**, in which nothing more interesting than damping in the two SLE's is seen: the damping is faster as predicted by the new SLE because of the existence of an additional channel for the removal of the energy of the quasiparticle. In **b**, however, $\chi/2V$ equals 1.25 and a sharp difference emerges in the predictions of the two SLE's: the new SLE drives the evolution towards the stationary state while the old SLE merely exhibits damped oscillations

the onset of self-trapped states, and the value 2 is the minimum value required to trap an initially fully localized quasiparticle (see [8] for a complete discussion). The relaxation rate Γ in Fig. 1, in units of $2V$, is 3. The relaxation is thus neither too fast nor too slow. The value of the fluctuation (dephasing) rate α , in units of $2V$, is 4×10^{-3} .

The same value of the nonlinearity is used in Fig. 2 as in Fig. 1. However, the relaxation rate Γ is taken to be 10 times larger: $\Gamma/2V=30$. The dephasing rate α is taken to be $(2V)$ times 0.4×10^{-3} in Fig. 2a but 16 times larger in Fig. 2b. Interesting structure in the evolution is apparent in the slow dephasing case of Fig. 2a but not in the fast dephasing case of Fig. 2b. In Fig. 2a, one sees not only the processes of self-trapping into the localized state and of the destruction of that state as

in Fig. 1, but also two separate phases of the first process. In the first phase the probability difference oscillates around the value 0, there being no clue of self-trapping in the time evolution. This phase ends at about $t=20/V$ and then the localized state begins to be formed. The destruction of that state occurs between $t=60/V$ and $t=125/V$. These three time regions are marked by arrows in Fig. 2a. By contrast, nothing richer than oscillations that are damped out to the value 0 is seen in Fig. 2b, whose parameter values are the same as those for Fig. 2a except for $\alpha/2V$, which equals 6.4×10^{-3} . The dephasing is so strong that it masks the formation of the localized state. Figure 3 shows the intermediate case: $\chi/2V=1.25$ and $\Gamma/2V=30$ as in Fig. 2a and b, but the dephasing rate α , in units of $2V$, equals 1.6×10^{-3} . All three phases of the evolution are completely clear in Fig. 3. Even the final destruction of the localized state is essentially complete by $t=125/V$.

The question of the validity of the SLE used in [1], which provided the initial motivation for the present investigation, is answered pictorially in Figs. 4 and 5. The main feature of the new SLE (12), which is absent in the earlier SLE (2), consists of the nonadiabatic characteristics (non-infinite relaxation) introduced in [9]. The new SLE (solid lines in Figs. 4 and 5) is therefore capable of exhibiting the formation of the localized state, while the old SLE (dashed lines in Figs. 4 and 5) is not. Both describe dephasing in the same way. The difference is, therefore, expected to be small for large α . Figure 4a and b show this to be true. In both cases, fast relaxation is considered ($\Gamma/2V=40$), and $\alpha/2V$ equals 6.4×10^{-3} . The nonlinearity ratio $\chi/2V$ is 2.1 in Fig. 4a and 4 in Fig. 4b. Little qualitative difference exists between the predictions of (2) and (12), particularly in Fig. 4b. The adiabatic SLE generally predicts slower damping because it lacks the additional damping agent (removal of energy from the quasiparticle by the vibrations) which the new SLE possesses. This difference in the damping times can be also seen in Fig. 5 where a slower dephasing rate ($\alpha/2V=4 \times 10^{-4}$) has been assumed. The relaxation rate Γ , in units of $2V$, is 20 both in Fig. 5a and b. The nonlinearity ratio $\chi/2V$ is 1 in Fig. 5a and nothing more than damping is seen from both equations. However, in Fig. 5b, where the nonlinearity is 1.25, the richer nature of the new SLE is obvious: it drives the evolution of the system towards its stationary state while the old SLE merely exhibits damped oscillations.

4. Discussion

The general issues under investigation in the present paper concern the transport of a quasiparticle moving in a crystal and interacting strongly with vibrations, the relaxation rates being finite and the temperature being non-zero. The particular system studied is a dimer. The point of departure for the analysis presented is a combination of the physics presented in [8] and [9] on the one hand, and the stochastic techniques presented in [10] on the other. Equations (6) and (7) above describe that combination. The main new results we have ob-

tained are in (8), (9) and (12) and in Figs. 1–5. Equation (8) is an exact consequence of (6) and (7), whereas (12) is obtained as an approximation. The approximation consists of the assumption (10). It is a near-equilibrium approximation and its reliability generally increases as the temperature is increased. Our central result (12), while based on approximations such as (10), possesses many of the essential features necessary for the description of the quasiparticle transport, and we suggest that it be used for the analysis of nonlinear transport in the same role as played by the linear SLE in linear transport situations such as in earlier treatments of exciton dynamics in molecular crystals and aggregates [3–7]. We also present the generalization of (12), first for an infinite chain with nearest neighbor interactions:

$$\begin{aligned}
 id\rho_{mn}/dt = & V(\rho_{m+1n} + \rho_{m-1n} - \rho_{mn+1} - \rho_{mn-1}) \\
 & - \chi(\rho_{mm} - \rho_{nn})\rho_{mn} - i(\chi V/\Gamma)\rho_{mn}(\rho_{m+1m} \\
 & + \rho_{m-1m} - \rho_{mm+1} - \rho_{mm-1} - \rho_{n+1n} - \rho_{n-1n} \\
 & + \rho_{nn+1} + \rho_{nn-1}) \\
 & - i\alpha(1 - \delta_{mn})(\rho_{mn} - \rho_{mn}^{\text{eq}}) \quad (13)
 \end{aligned}$$

and then for an arbitrary crystal as in (1), m, n being vectors of appropriate dimensions:

$$\begin{aligned}
 id\rho_{mn}/dt = & [V, \rho]_{mn} - \chi(\rho_{mm} - \rho_{nn})\rho_{mn} \\
 & - i(\chi/\Gamma)\rho_{mn}([V, \rho]_{mm} - [V, \rho]_{nn}) \\
 & - i\alpha(1 - \delta_{mn})(\rho_{mn} - \rho_{mn}^{\text{eq}}) \quad (14)
 \end{aligned}$$

These generalizations are obtained by replacing the probabilities $\rho_{mm}(t)$ and $\rho_{nn}(t)$ in the nonlinear term (second term on the right hand side of (1)) by their respective values at a time $t - 1/\Gamma$, and then using a large Γ approximation. This delay or lag is an effect of finite relaxation and has been explained in detail in [9]. The thermal fluctuation effect is taken for simplicity to be the same as in the dimer case: the off-diagonal elements of the density matrix are driven to their equilibrium values ρ_{mn}^{eq} at the dephasing rate α .

The time evolution of the discrete nonlinear Schrödinger equation for the two-site system [2, 8–10, 12, 13] was analyzed in the adiabatic case in [2], [8] and in the nonadiabatic case in [9]. The augmentation of the former through damping terms was treated in [1]. The resulting equation, viz. (2), showed nonlinear evolution at short times, and damping and equilibration between the two sites for long times, but was unable to describe the formation of the localized states [1]. The description of such a formation process was natural to the analysis of Kenkre and Wu [9] who presented a physically sound mechanism of the removal of energy from the quasiparticle through its interaction with the vibrations. The generalizations of the analysis of [9] to finite temperatures, carried out by Grigolini et al. [10] provided us with the necessary tools to investigate the validity of the SLE of [1]. The primary result we have obtained in the present paper on that basis is the new SLE (12) (or its more general versions (13) and (14)). It describes the evolution of the complete density matrix in the presence of strong

interactions with vibrations and, unlike earlier transport instruments, is *not* limited to the case of infinitely fast relaxation (as is [1]) or to zero temperature (as is [9]).

The new SLE we present has two kinds of terms: those which explicitly describe the finite-rate relaxation process and, therefore, clearly show the formation of the localized self-trapped states provided the nonlinearity is strong enough; and those which are responsible for the subsequent destruction of the self-trapped states through thermal fluctuations. Figures 1–3 make this clear. We would like to draw the attention of the reader particularly to Figs. 1 and 3, which clarify the unified description that our SLE provides for all the important phases of time evolution: the pre-trapping oscillations of the probability, the formation of the self-trapped state, and the destruction of self-trapping through overbarrier motion.

Our results concerning the validity of the old SLE are displayed in Figs. 4, 5. Our analysis has given the following answers to the questions posed in Sect. 1. The adiabatic SLE of [1] can be naturally combined with the nonadiabatic analysis of [1] through a stochastic theory of the interactions of the quasiparticle with a bath as shown here and in [10]. The adiabatic SLE need not be regarded as the result of an ad hoc augmentation of the discrete nonlinear Schrödinger equation but constitutes a well-defined limiting case of the new nonadiabatic stochastic Liouville equation. The latter can be derived from the Fokker-Planck treatment, as we have shown here, with the help of the high damping assumption and the factorization procedure. While the nature of the derivation of (12) we have provided here makes it questionable for temperatures which are small enough to violate the approximation (10), we suggest that it may be feasible to use (12) even for intermediate temperatures, changing only the expression for the dephasing rate α , given in (9). This suggestion is no more than an interpolation idea but has, for its support, the fact that (12) *does* appear to provide the qualitatively correct time evolution in all cases. We hope to report, on the basis of a study of the coupled hierarchy of the moments of the distribution function, detailed investigations of these conjectures in the near future.

We mention in passing a rather interesting feature of the equilibrium distribution (11) we have obtained above. In the case of the *linear* dimer, $\chi=0$, and (11) shows that the equilibrium value of r is the Langevin function $L(V/k_B T)$

$$r_{\text{eq}} = (\rho_{12} + \rho_{21})_{\text{eq}} = L(V/k_B T) = \coth(V/k_B T) - (k_B T/V). \quad (15)$$

This result is to be expected in the light of the representation [14, 15] of a two-state quantum mechanical system by a dipole rotating in three dimensions [11]. However, r_{eq} , which is nothing but the difference in the probabilities of occupation of the stationary states $|\pm\rangle \equiv (\frac{1}{2})^{-\frac{1}{2}}(|1\rangle \pm |2\rangle)$ of the linear dimer, should be given by the quantum mechanical equilibrium value

$$r_{\text{eq}} = \tanh(V/k_B T). \quad (16)$$

Both (15) and (16) have the same qualitative shape but they certainly differ quantitatively. The difference stems from the fact that we have not used the second postulate of quantum statistical mechanics [16], viz. the assumption of random phases, in our derivation of (15). That derivation treats a classical bath in interaction with a quantum mechanical dimer. When the second postulate is invoked through the construction of an ensemble, (15) does indeed reduce to the correct quantum mechanical result (16). Further subtleties are being worked on and will be reported in the near future [17].

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